Short communication

An imidazolium-based polymerized ionic liquid via novel synthetic strategy as polymer electrolytes for lithium ion batteries

Kun Yin [a], Zhengxi Zhang [a], Li Yang [a,b,*], Shin-Ichi Hirano [b]

[a] School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China
[b] Hirano Institute for Materials Innovation, Shanghai Jiao Tong University, Shanghai 200240, PR China

HIGHLIGHTS

- An imidazolium-based PIL is successfully obtained via new synthetic strategy.
- Based on the PIL host, flexible polymer electrolyte membranes are prepared.
- The polymer electrolytes show excellent electrochemical performance.

ARTICLE INFO

ABSTRACT

An imidazolium-based polymerized ionic liquid (PIL), poly(1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonylimide)) is successfully synthesized via a new three-step process comprising the direct radical polymerization of the 1-vinylimidazole monomer, and subsequent quaternization reaction followed by an anion exchange procedure. Furthermore, polymer electrolytes are prepared by blending as-obtained PIL as the polymer host with an ionic liquid and LiTFSI salt. Electrochemical measurements demonstrate that compared with polymer electrolytes containing the PIL host synthesized by the conventional route, polymer electrolytes containing the PIL host obtained by new synthetic process exhibit significantly improved capacity and cycling performance, which is due to higher ionic liquid content.

1. Introduction

Polymerized ionic liquids (PILs) display interesting properties as film forming ability, easy handling, good electrochemical performance and chemical compatibility toward ionic liquids (ILs) [1,2], so they have been considered as the host in a new class of safe polymer electrolytes, which may be applied in energy storage and conversion systems, such as lithium ion batteries, quasi-solid-state dye-sensitized solar cells, and fuel cells [2–4]. Ohno et al. have firstly prepared various PILs, and systematically investigated the impact of the structural parameters of PILs, such as cation structure, anion species and the presence of networks on the thermal and ionic conductivity characteristics [5,6]. Other research groups, such as groups of Mecerreyes [1,7], Long [8], Shaplov [9], Koo [10], etc.

have also reported that the thermal and electrochemical properties of PILs change widely as a function of cation structure and/or counteranions. Moreover, polymer electrolytes based on a PIL as the host in combination with an ionic liquid and a lithium salt have been investigated as promising electrolytes for lithium ion batteries [11–14]. In spite of extensive reports about properties of PILs, and a few reports about application of PILs in lithium ion batteries, researches involving polymer electrolytes with an imidazolium-based PIL host for lithium ion batteries are quite rare.

At the present time, there are several strategies towards developing PILs, and the most common approach involves the direct radical polymerization of IL monomers [15]. Taking 1-vinylimidazolium-based IL monomers for example, the conventional route is outlined in Fig. 1(a). It should be noted that such route often yields low molecular weight PILs, which would be disadvantageous to the properties of PILs [15,16]. From a synthetic perspective, the approach affect the molecular weight of PILs, thus affect the properties of PILs [15]. In order to further improve PILs properties, it is important to develop PILs by utilizing new synthetic routes.

* Corresponding author. School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China. Tel.: +86 21 54748917; fax: +86 21 54741297.

E-mail address: liyangce@sjtu.edu.cn (L. Yang).
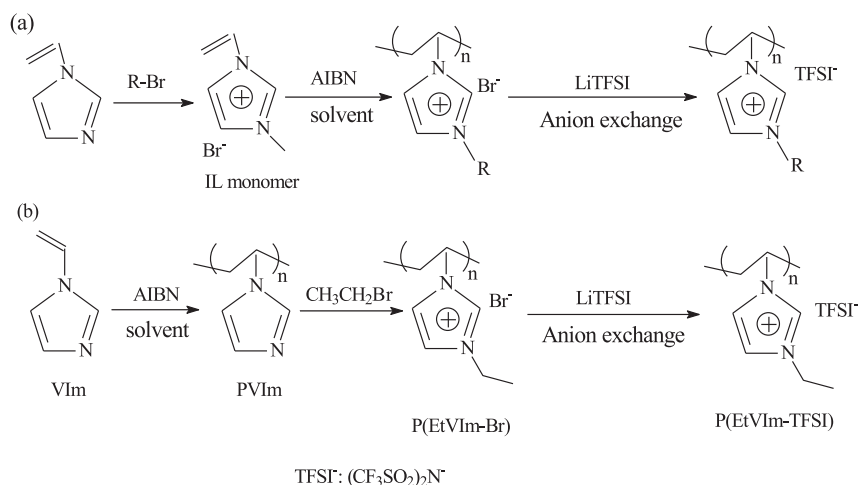
Fig. 1. (a) The conventional synthetic route of the imidazolium-based PIL and (b) new synthetic route of the imidazolium-based PIL proposed in this work.

In this article, we synthesized an imidazolium-based polymerized ionic liquid (PIL), poly(1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonylimide)) (P(EtVIm-TFSI)), via a new three-step process, as outlined in Fig. 1(b). For comparison with new synthetic strategy, P(EtVIm-TFSI) was also synthesized through the conventional route. Subsequently, polymer electrolyte membranes were obtained by incorporating the PIL as the host, an ionic liquid and LiTFSI salt. The electrochemical properties for as-obtained polymer electrolytes were studied to evaluate their potential use in lithium ion batteries.

2. Experimental

2.1. Materials

1-Vinylimidazole (VIm) (98%) and 1, 2-dimethylimidazole (98%) were purchased from J&K Chemical. Bromoethane and 2,2′-azobis(isobutyronitrile) (AIBN) were purchased from Aladdin, and AIBN was recrystallized from ethanol. 2-Bromoethyl ethyl ether (98%) was purchased from Energy Chemical. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) was kindly provided by Morita Chemical Industries Co., Ltd. All other reagents were used as received.

2.2. Synthesis of imidazolium-based PIL, (P(EtVIm-TFSI))

P(EtVIm-TFSI) was synthesized via a new three-step process. In the first step, the PVIm homopolymer was obtained by radical polymerization of VIm in toluene with AIBN as an initiator (0.5 wt.% with respect to monomer) under Ar at 65 °C for 8 h. Subsequently, the bromide intermediate, P(EtVIm-Br) was synthesized by refluxing the mixture of PVIm (1 equiv. with respect to monomer unit) and bromoethane (3 equiv.) in a methanol solution for 20 h at 50 °C. Finally, the resulting P(EtVIm-TFSI) was synthesized by anion exchange reaction of P(EtVIm-Br) (1 equiv. with respect to monomer unit) with LiTFSI (1.2 equiv.).

P(EtVIm-TFSI) was also synthesized by the conventional route reported previously [8].

In the following, the PILs obtained by new and conventional routes were denoted as PIL(NR) and PIL(CR), respectively.

2.3. Synthesis of an IL, 1,2-dimethyl-3-ethoxyethyl imidazolium bis(trifluoromethanesulfonyl) imide (IM(2o2)11TFSI)

IM(2o2)11TFSI was synthesized according to procedures reported previously [17], and its chemical structure was confirmed by the ^{1}H NMR spectrum.

2.4. Preparation of polymer electrolyte membranes based on PIL, P(EtVIm-TFSI) as the host

The polymer electrolyte membranes with different weight compositions (Table 1) were prepared by dissolving the as-obtained PIL (host), IM(2o2)11TFSI (ionic liquid) and LiTFSI (salt) in acetonitrile. The solutions were casted into PTFE molds to prepare the electrolyte films. The films were dried in the Ar atmosphere at room temperature for 16 h, and subsequently dried under vacuum at 90 °C for 24 h. Finally, the films were dried in an argon-filled glove box ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) for 48 h in order to remove the final traces of acetonitrile.

2.5. Test cells assembly

The cathode was obtained by blending 80 wt.% $LiFePO_4$ with 10 wt.% acetylene black and 10 wt.% poly(vinylidene fluoride) (PVDF). The active material loading was about 2.5 mg cm^{-2}. Lithium metal foil (battery grade) was used as the anode. The CR2016 coin-type cells were fabricated by laminating a $LiFePO_4$ cathode, a polymer electrolyte membrane and a lithium metal anode in an argon-filled UNILAB glove box.

Table 1
Composition of polymer electrolyte membranes.

Sample	Weight composition (wt. %)			
	PIL(NR) (host)	PIL(CR) (host)	IM(2o2)11TFSI (ionic liquid)	LiTFSI (Li salt)
PIL(NR)-LiTFSI-IL-55%	100	–	55	20
PIL(NR)-LiTFSI-IL-60%	100	–	60	20
PIL(NR)-LiTFSI-IL-65%	100	–	65	20
PIL(CR)-LiTFSI-IL-45%	–	100	45	20

2.6. Measurements

The chemical structures of polymers prepared in this work were confirmed by ^{1}H NMR (Avance III 400) technique. Elemental composition (C, N and S) was determined by an elemental analyzer (Elementar, Vario-ELIII IRMS).

The ionic conductivity of polymer electrolyte membrane was determined by impedance measurements using a CHI660B Electrochemical Workstation from 25 to 80 °C. The data were collected over a frequency range 1 Hz−100 kHz with amplitude of 5 mV for an open circuit potential at various temperatures. The ionic conductivity (σ) of these electrolytes was calculated according to the following equation:

$$\sigma = \frac{L}{R \cdot S}$$

Here, R is the bulk electrolyte resistance, L and S are the thickness and area of the polymer electrolyte film, respectively.

The electrochemical stability of polymer electrolytes was examined by linear sweep voltammetry (LSV) at 60 °C (scan rate 10 mV s^{-1}) using the stainless steel (SS)/PIL-based electrolyte/Li cell, in which the SS was used as working electrode and lithium metal was used as both counter and reference electrodes.

The cycling tests on Li/PIL-based electrolyte/LiFePO$_4$ batteries at 60 °C were performed at 0.1 C current rate between 2.5 V and 4.0 V.

3. Results and discussion

The chemical structures of PVIm and PIL (P(EtVIm-TFSI)) obtained through the new synthetic route are confirmed by the ^{1}H NMR spectra, as displayed in Fig. 2. In the spectrum of the PVIm homopolymer (Fig. 2(a)), the signals attributing to the polymer backbone protons appear between 1.6 and 3.5 ppm, while the signals around 6.2 and 7.0 ppm correspond to the imidazolium ring protons. The VIm monomer has double bond signals at around 4.7, 5.1, and 6.7 ppm (data not shown), and the signals disappear after polymerization, indicating that the VIm monomer is completely polymerized. After quaternization and anion exchange reaction of PVIm, the structure of the polymer backbone is maintained, as shown in Fig. 2(b). The signals at 6.7−7.0 ppm (1H), 7.2−7.5 ppm (1H), and 8.2−8.6 ppm (1H) represent the three protons in the
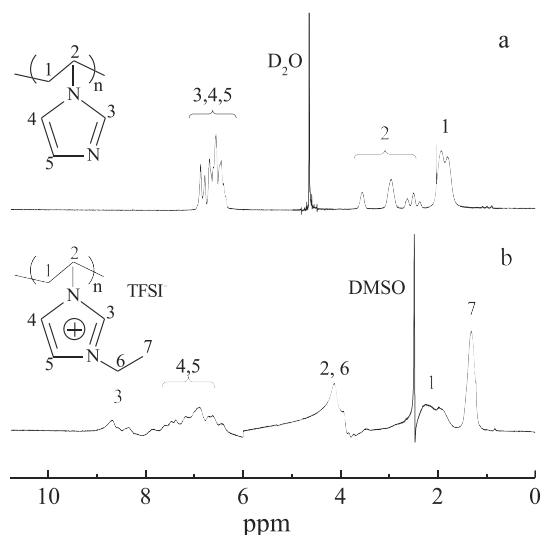
imidazole ring. Besides, the signals of ethylene protons (−CH$_2$CH$_3$) in side chain can be found at around 1.3 and 4.1 ppm. Therefore, the ^{1}H NMR spectra of PVIm and P(EtVIm-TFSI) are in good agreement with the expected structure. Moreover, the elemental analysis result for PIL (Anal. Found: C 28.55, N 11.02, S 15.04. Anal. Calcd.: C 26.80, N 10.42, S 15.90) also proves high purity.

The temperature dependence of ionic conductivity (σ) for the polymer electrolytes based on the PIL host, which has been obtained by the new route, is depicted in Fig. 3(a). It is clear that for three electrolyte samples, ion conductivity increases with the increase of temperature, arising from faster movement of the ions and easier mobility of PIL segments. It can also be found that an increase in the content of IM(2o2)11TFSI leads to the enhancement of the conductivity, which is ascribed to that increasing IM(2o2)11TFSI content can accelerate the segmental motion of the PIL chains, thus improve ion-transporting ability and subsequently raise ion conductivity. The PIL(NR)-LiTFSI-IL-65% sample shows an ionic conductivity of 1.89×10^{-5} S cm^{-1} and 1.84×10^{-4} S cm^{-1} at 25 °C and 60 °C, respectively. Note that as the IM(2o2)11TFSI content is increased above 65 wt.%, the membranes are sticky and quite difficult to handle. Fig. 3(b) shows linear sweep voltammograms of polymer electrolytes at 60 °C, obtained from the SS/PIL electrolyte/Li cell. It can be observed that the electrochemical stability of the PIL-based electrolytes are not obviously affected by the IM(2o2)11TFSI content. The three electrolyte samples all have good electrochemical stability, and decompose at about 4.5 V (vs. Li/Li$^+$), which corresponds to the anodic electrochemical stability limit.
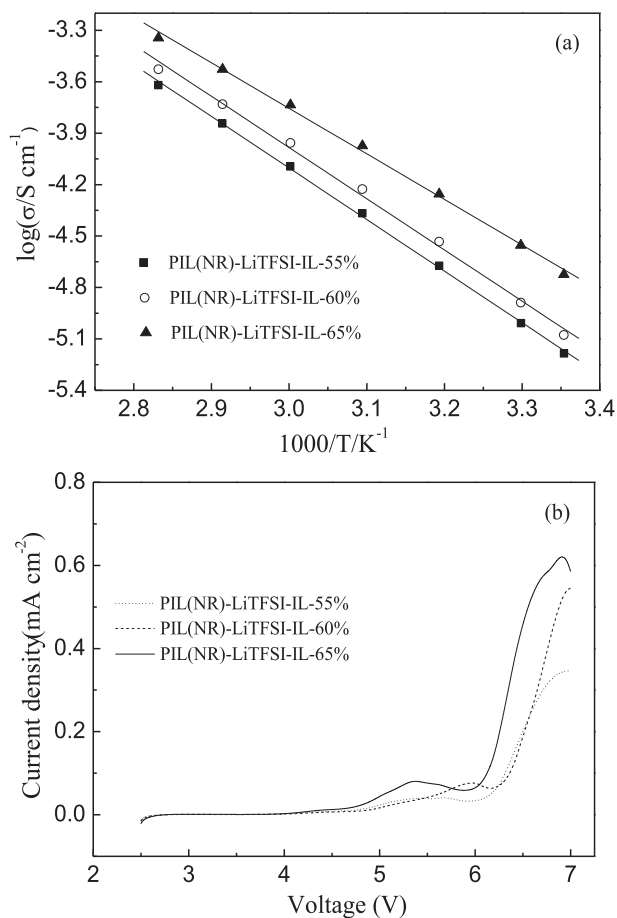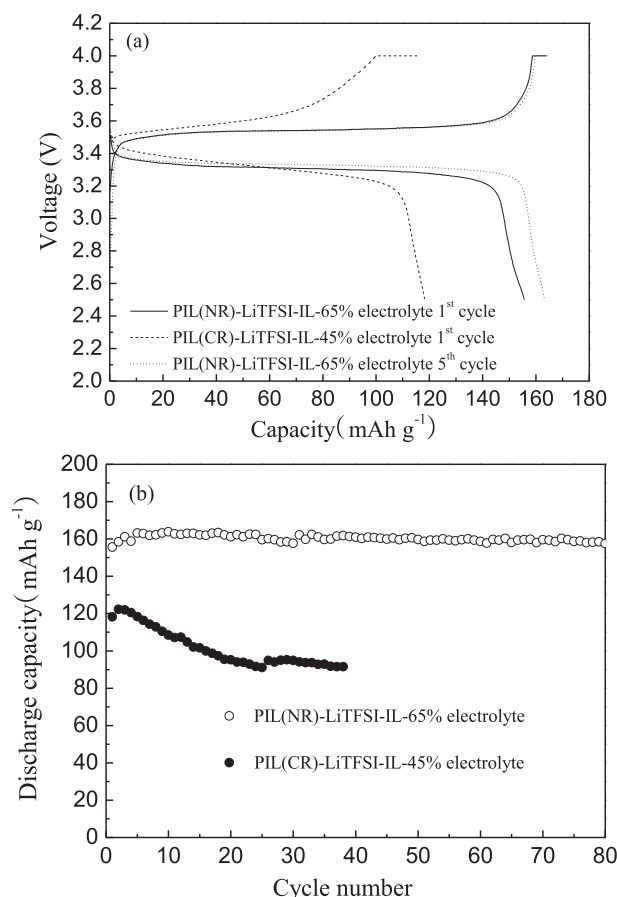

Fig. 3. (a) Temperature dependence of ionic conductivity for polymer electrolytes with different IM(2o2)11TFSI contents and (b) linear sweep voltammograms of polymer electrolytes with different IM(2o2)11TFSI contents at 60 °C (SS/PIL electrolyte/Li cells, 10 mV s^{-1}, 2.5−7.0 V).

Fig. 2. ^{1}H NMR spectra of (a) the PVIm in D$_2$O and (b) the PIL (P(EtVIm-TFSI)) in DMSO-d_6.

Fig. 4. Cell performance of Li/LiFePO₄ cells containing PIL(NR)-LiTFSI-IL-65% and PIL(CR)-LiTFSI-IL-45% electrolytes at 60 °C (2.5–4.0 V): (a) charge/discharge curves for selected cycles and (b) discharge capacities as a function of the cycle number. Charge–discharge current rate: 0.1 C.

This indicates that the PIL-based electrolytes mentioned above could be suitable for application as promising electrolytes for lithium ion batteries.

In the case of the PIL host synthesized by the conventional route, the maximum IM(2o2)11TFSI content in the polymer membranes is about 45 wt.% (with respect to host), and the corresponding polymer electrolyte is denoted as PIL(CR)-LiTFSI-IL-45%. In the following, PIL(NR)-LiTFSI-IL-65% and PIL(CR)-LiTFSI-IL-45% electrolytes are tested in Li/LiFePO₄ cells.

Fig. 4(a) shows the charge/discharge curves of the Li/LiFePO₄ cells containing the PIL(NR)-LiTFSI-IL-65% and PIL(CR)-LiTFSI-IL-45% electrolytes in the selected cycles at 60 °C. The cells with PIL(NR)-LiTFSI-IL-65% and PIL(CR)-LiTFSI-IL-45% electrolytes delivers initial discharge capacities of 155.6 mAh g^{-1} and 118.3 mAh g^{-1} at 0.1 C current rate, respectively. In the case of the cell with the PIL(NR)-LiTFSI-IL-65% electrolyte, the charge/discharge curve displays a flat plateau at 3.5 V and 3.4–3.3 V, which is a typical characteristic of Li/LiFePO₄ cells [18]. Moreover, the cell delivers a stable discharge capacity after 5 cycles. Fig. 4(b) demonstrates the cycling performance of the Li/LiFePO₄ cells. For the cell containing the PIL(NR)-LiTFSI-IL-65%, during the initial several cycles, the discharge capacity increases, perhaps resulted from the optimization of the electrolyte/electrode interfaces [19], which is similar to some other reported gel polymer electrolytes [12]. After an initial increase, the cell can achieve discharge capacity of about 160 mAh g^{-1}, which is close to the theoretical capacity (170 mAh g^{-1}). Moreover, the discharge capacity of 157.5 mAh g^{-1}

(92.6% of the theoretical value) can still be retained after 80 cycles. On the other hand, the cell with the PIL(CR)-LiTFSI-IL-45% only delivers discharge capacity of about 120 mAh g^{-1}, and has capacity fade on cycling. The result indicates that the PIL(NR)-LiTFSI-IL-65% electrolyte shows obviously better discharge capacity and capacity retention than the PIL(CR)-LiTFSI-IL-45% electrolyte, attributing to higher IL content in the PIL(NR)-LiTFSI-IL-65% electrolyte, which may be associated with higher molecular weight of the PIL host synthesized by the new synthetic route. Unfortunately, using gel permeation chromatography could not provide any useful data for the molecular weight of the imidazolium-based PIL due to polymer aggregation and column interaction [8]. Recently, some polymer electrolytes containing a PIL as the host with an ionic liquid and LiTFSI salt have been prepared and applied in lithium ion batteries [11–14]. Appetecchi et al. [11] firstly investigated the application of polymer electrolytes containing pyrrolidinium-based PILs as polymer host in lithium ion batteries. The Li/LiFePO₄ cells are capable to deliver above 140 mAh g^{-1} at 0.1 C current rate at 40 °C. It should be noted that the cathode contains 43 wt.% LiFePO₄ active material, which is relatively low for lithium batteries. Later, Li et al. [12,13] reported that Li/LiFePO₄ cells with polymer electrolytes containing guanidinium-based PILs prepared by the conventional route as polymer hosts can deliver discharge capacities of about 140 mAh g^{-1} at 0.1 C rate at 80 °C. Subsequently, Li et al. [14] further developed polymer electrolytes based on tetraalkylammonium-based PIL as the host, and the cell test showed that Li/LiFePO₄ cells had discharge capacity of 122 mAh g^{-1} at 0.1 C rate at 60 °C.

4. Conclusions

An imidazolium-based polymerized ionic liquid (PIL), poly(1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonylimide)) is obtained through a new three-step route. Moreover, polymer electrolytes based on the as-obtained PIL host in combination with an ionic liquid and LiTFSI salt have been prepared. The cell tests show that the Li/LiFePO₄ cell assembled with the above polymer electrolytes at 60 °C exhibits higher discharge capacity and capacity retention at a current rate of 0.1 C than the cell with polymer electrolytes containing the PIL host synthesized by the conventional route. This result should be attributed to higher ionic liquid content in the polymer electrolytes containing the PIL host obtained by the new synthetic route.

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